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Several enchancements were made to our program for calculating the nonlinear optical properties (hyperpolarizabilities) of molecules based on the Time-Dependent Hartree-Fock procedure. The major extension was the inclusion of solvent effects with the use of a self-consistent reaction field approach. This method has been tested on a few small molecules and further testing is underway. Other improvements were made that primarily related to ease of use and efficiency of the program.

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Extensions to Hyperpolarizability Calculations

AASERT Final Report

The goal of this work was to develop fast efficient computational procedures for obtaining accurate estimates of molecular nonlinear optical properties.

I. Background

The polarization, *P*, induced in a medium by an external electric field E is given by

$$P = P^0 + \chi^{(1)} \cdot E + \chi^{(2)} \cdot E \cdot E + \chi^{(3)} \cdot E \cdot E \cdot E + \cdots \qquad (1)$$

where $\chi^{(n)}$ are the nth order susceptibility tensors of the bulk medium. Nonlinear optical properties of substances arise from nonzero values of terms higher than $\chi^{(1)}$. These bulk susceptibilities can be expressed in terms of the molecular induced dipole. The dipole moment of a system interacting with an electric field can be written

$$\mu_i = \mu_i^0 + \alpha_{ij} E_j + \frac{1}{2!} \beta_{ijk} E_j E_k + \frac{1}{3!} \gamma_{ijkl} E_j E_k E_l + \cdots \qquad (2)$$

where μ_j^0 is the permanent dipole moment and α_{ij}, β_{ijk}, and γ_{ijkl} are tensor elements of the polarizability, first hyperpolarizability and second hyperpolarizability, respectively. In the above expression the Einstein convention of summation over repeated indices is assumed.

As an efficient method for the calculation of frequency dependent properties at the Hartree-Fock level, we have implemented the "any-order" TDHF procedures of Sekino and Bartlett[1] and Karna and Dupuis[2]. Our initial TDHF codes have been implemented and distributed as part of the MOPAC semiempirical program as part of MOPAC93[3] and as part of the GAMESS program package.[4] The semiempirical program is designed to study systems too large for the current *ab initio* programs. The distributed versions of the TDHF program are capable of calculating the quantities listed below:

Property	Name	Abbreviation Used
$\alpha(-\omega;\omega)$	Frequency Dependent Polarizabilities	
$\beta(-2\omega;\omega,\omega)$	Second Harmonic Generation	SHG
$\beta(-\omega;0,\omega)$	Electrooptic Pockels Effect	EOPE

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$\beta(0;-\omega,\omega)$	Optical Rectification	OR
$\gamma(-3\omega;\omega,\omega,\omega)$	Third Harmonic Generation	THG
$\gamma(-2\omega;0,\omega,\omega)$	DC-Electric Field Induced	
	Second Harmonic Generation	EFISH
$\gamma(-\omega;\omega,-\omega,\omega)$	Intensity Dependent Index of Refraction	IDRI
	(also Degenerate Four-Wave Mixing)	DFWM
$\gamma(-\omega;0,0,\omega)$	Optical Kerr Effect	OKE

The TDHF procedure in GAMESS is capable of performing both semiempirical (AM1 and PM3) and *ab initio* calculations. Furthermore, the *ab initio* version of the TDHF code is implemented as both a conventional SCF procedure based on previously calculated and stored two-electron integrals and a direct SCF procedure in which the integrals are calculated as needed and not stored. This latter procedure is necessary for large basis sets. We have also implement the parallel computer capabilities of GAMESS into the TDHF code and this procedure runs on a wide variety of parallel computers. The combination of parallel and direct TDHF now allow system of experimental interest to be studied and this forms the basis of our ongoing research. This program is now a tool for general use.

II. Solvent Effects

Solvent effects are important for solution phase hyperpolarizabilities. One method to take solvent effects into account is via the "reaction field" (RF) model first proposed by Onsager[5]. In this model, the molecule of interest (the solute) is put in a cavity surrounded by a continuous medium (the solvent) with a fixed dielectric constant, ε. This procedure has been implemented within the framework of both semiempirical programs[6-8] and *ab initio* programs[9] to predict solvent effects on conformational and isomerization energies and electronic and vibrational spectra. We have implemented this procedure is our TDHF programs to study solvent effects on the hyperpolarizabilities of molecules.

The electrostatic solvent effects are included by an additional perturbation term, H', in the Hamiltonian, which describes the coupling between the molecular dipole ($\bar{\mu}$) and the reaction field ($\bar{R}$) as

$$H' = -\bar{\mu} \cdot \bar{R} .\tag{3}$$

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The reaction field is, in turn, proportional to the molecular dipole

$$\vec{R} = g \cdot \vec{\mu} , \tag{4}$$

where g depends on the dielectric constant of the medium and cavity size. For a spherical cavity

$$g = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)a_0^3} , \tag{5}$$

where a_0 is the cavity radius.

Using this term in the variational procedure, we obtain

$$F = h_0 - \mu \bullet g \bullet < \psi | \hat{\mu} | \psi > + D(2J - K) \tag{6}$$

as the expression for the Fock matrix with the SCRF perturbation included. For purposes of evaluation, the dipole portion can be separated into nuclear and electronic contributions as

$$F = h_0 - \mu \bullet g \bullet Tr\{\mu_{elec}D\} - \mu \cdot g \cdot \mu_{nuc} + D(2J - K) \tag{7}$$

utilizing the property that the trace of an operator with the density matrix yields the expectation value for the operator. This allows a straightforward evaluation of the new Fock matrix using available matrices within the code.

The solution presented above is valid for the zeroth order TDHF solution, however the perturbation term must be reexamined for higher order expressions. Consider the first order TDHF equations. Taking the derivative of equation (7) with respect to the applied field along the a direction (where $a \in \{x, y, z\}$), yields the following expression for F^a:

$$F^a = -\mu \bullet g \bullet Tr\{\mu^a_{electronic} D^0 + \mu^0_{electronic} D^a\} - \mu \bullet g \bullet \mu^a_{nuclear} + D^a(2J - K). \tag{8}$$

With the nuclei fixed, the derivative of the nuclear part of the dipole moment operator is equal to zero, giving the first order expression

$$F^a = -\mu \bullet g \bullet Tr\{\mu_{electronic} D^a\} + D^a(2J - K). \tag{9}$$

Applying the same procedure, the expressions for the higher order terms (through third order) are found to be

$$F^{ab} = -\mu \bullet g \bullet Tr\{\mu_{electronic} D^{ab}\} + D^{ab}(2J - K), \tag{10}$$

$$F^{abc} = -\mu \bullet g \bullet Tr\{\mu_{electronic} D^{abc}\} + D^{abc}(2J - K). \tag{11}$$

Results

Our preliminary results are based on four small, test molecules - HF, H_2O, HCN, and CH_3CN. In this study, we employed four different basis sets: 2 "normal" quantum chemical basis sets (6-31G**[10] and cc-pVDZ[11]) and 2 "NLO" basis sets (Sadlej[12] and POL+[13]). The POL+ basis set is the same as Sadlej's polarization basis set with the addition of a set of d functions on all hydrogens.

A summary of our findings is shown in the following figures, which compare the isolated molecule (gas) results with the SCRF-TDHF results (solution) for the two larger basis sets. A complete set of results given in the appendix. All SCRF calculations were done with a dielectric constant of 80, approximately the value of water.

Alpha

First Hyperpolarizability

Second Hyperpolarizability
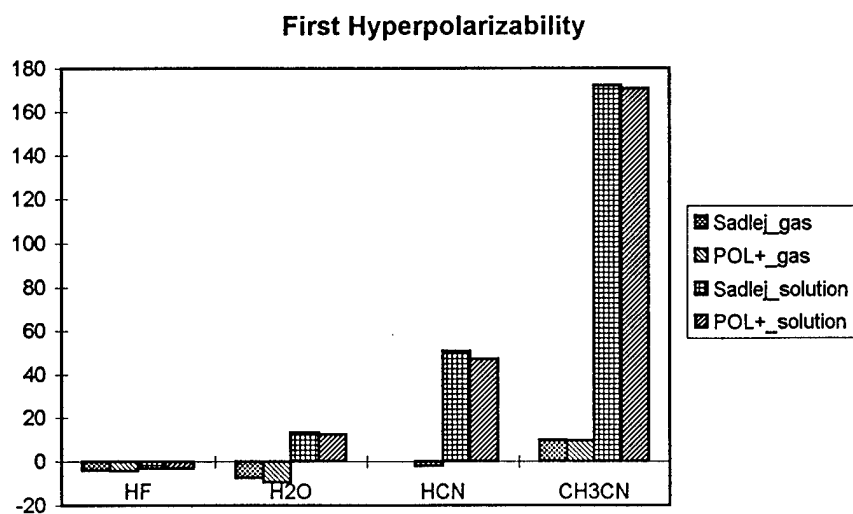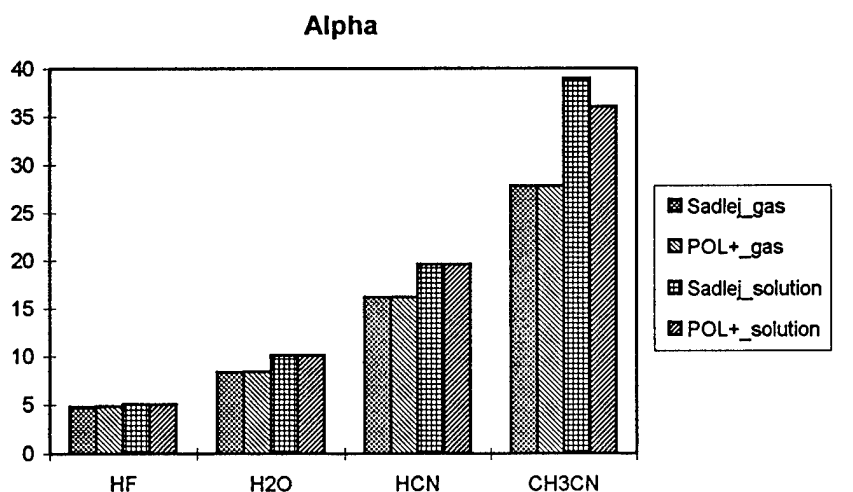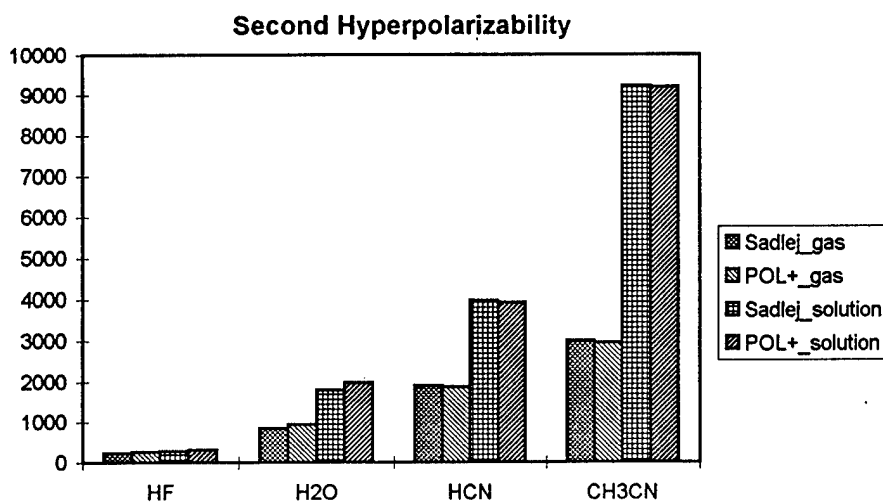
The solvent effects on the hyperpolarizabilities (β and γ) are clearly much larger than for the polarizability (α). Of the hyperpolarizabilities, β is more interesting in that 1) the solvent effects are very large, 2) the solvent sometimes causes are reversal of sign of β, and 3) basis set effects are hard to converge. We are continuing our studies to larger, more experimentally reasonable systems with the goal of providing a benchmark of the accuracy of the method.

One problem with SCRF calculations in the arbitrary nature of the cavity. In this study we have used spherical cavities based on molar volumes or van der Waals radii. The next step is to improve the nature of the cavity by including higher moments in the interaction and/or using more realistic cavity shapes. All of these approaches have been implemented by others for ordinary SCF energy calculations and should be easy to implement in our TDHF-SCRF codes.

Another major problem, particular with solutes like those in our preliminary study, is the lack of specific solute-solvent interactions in the SCRF model. One method to work around this problem is to include several explicit solvent molecules in the cavity - thus obtaining the major short range and long range interactions. This approach was been taken by Mikkelsen et al.[14] in their RPA calculations and we are beginning similar calculations with our TDHF codes. The difficulties are in how many solvents to chose, where to put them, and what size of cavity to use.

III. Other TDHF Improvements

In addition to the TDHF-SCRF procedure, we have made other improvements in the TDHF code. One continuing problem with this type of TDHF procedure is its poor convergence.

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To help we have improved the code to use better initial guesses of starting matrices, implemented an extrapolation procedure for the "Fock" matrices, and tested a few DIIS procedures to help convergence. A great deal more needs to be done in this area and we are continuing to do so. One method currently under implementation is to solve a set of uncoupled TDHF-like equations and use these results as better initial guesses.

One further improvement to the GAMES TDHF code we have made is the ability to calculate all components of β and γ. With these results, it is possible to rotate the reference axes to either a) the moments of inertia, b) the optical axis (eigenvectors of α), or c) an arbitrary input set. The ability is necessary to allow the comparison of hyperpolarizability components between different calculations or during molecular transformations.

Our "new" versions of the TDHF code will be shortly send to Dr. Mark Gordon's group at Iowa State University for replacement of the older, less capable versions of the TDHF procedure in the available version of GAMESS.

We are also developing a complex version of the TDHF codes. An initial version of this code has been developed that uses fixed (input) damping factors and calculates the real and imaginary frequency dependent polarizabilities and hyperpolarizabilities. This work is in collaboration with Dr. Shashi Karna, USAF Philips Laboratory, New Mexico. Future work is also planed to go beyond TDHF and include electron correlation.

V. References

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VI. Personnel

This grant has been solely used to support a single graduate student - Antonio Ferreira, who should graduate with a Ph.D. in August 1997. It is his work that has been discussed in this report.

Several papers resulting from this support are in preparation and will be forwarded as soon as they are ready. Below is a list of conference presentations made by Antonio Ferreira while being supported by this grant.

February 1996   Poster at the 36th Sanibel Symposium, St. Augustine, FL, "A Self-Consistent Reaction Field Model for the Inclusion of Solvent Effects in TDHF Calculations of Hyperpolarizabilities".

December 1995   Talk at the SE/SW Regional ACS Meeting, Memphis, TN, "Calculations of Solvent Effects for Nonlinear Optical Properties".

August 1995   Poster at the 12th Canadian Symposium on Theoretical Chemistry, Fredericton, NB, "Solvent Effects in TDHF Calculations".

May 1995   Poster at the 24th Southeastern Theoretical Chemistry Association Conference, New Orleans, LA, "Corrections and Improvements to TDHF Calculations of NLO Properties".

August 1994   Talk at the 208th National American Chemical Society Meeting, Washington, DC, "Model Potential Studies of Hyperpolarizabilities".

November 1993   Poster at Current Trends in Computational Chemistry, Vicksburg, MS, "Can a Very Simple Model Give Reasonable Hyperpolarizabilities?".

Appendix

The following tables contain TDHF data for HF, H_2O, HCN, and CH_3CN for each of four basis sets. Data is given for molecular geometries obtained with and without the reaction field (labeled as SCRF and gas, respectively). For each input geometry, data is also given for calculations without the reaction field (gas), with the field (scrf), and a hybrid method based on using the reaction field in the reference calculation but not in the TDHF (zern). This last procedure is not a viable method.

Table 1: Static Polarizabilities

Molecule	Basis	Gas Geometry			SCRF Geometry		
		gas	zern	scrf	gas	zern	scrf
HF	6-31G**	2.6803	2.6476	2.7236	2.6875	2.6543	2.7309
	pVDZ	2.3432	2.3069	2.3688	2.3503	2.3135	2.3759
	Sadlej	4.8123	4.7990	5.0263	4.8230	4.8094	5.0378
	POL+	4.8363	4.8223	5.0519	4.8472	4.8328	5.0636
H_2O	6-31G**	4.8672	4.6984	5.2517	4.9170	4.7378	5.2996
	pVDZ	4.9334	4.7682	5.3340	4.9767	4.8041	5.3780
	Sadlej	8.3621	8.3630	10.0835	8.3851	8.3847	10.1152
	POL+	8.3947	8.3825	10.1115	8.4180	8.4045	10.1437
HCN	6-31G**	11.5677	11.4140	13.2422	11.6081	11.4525	13.2977
	pVDZ	12.1155	11.9187	13.8201	12.1578	11.9588	13.8775
	Sadlej	16.1595	16.2735	19.5169	16.2273	16.3414	19.6181
	POL+	16.1944	16.2909	19.5357	16.3414	16.3594	19.6378
CH_3CN	6-31G**	22.1579	22.0182	26.6923	22.2140	22.0712	26.7810
	pVDZ	22.7882	22.5712	27.4515	22.8448	22.6247	27.5396
	Sadlej	27.8142	28.1658	35.7934	27.9211	28.2768	38.9812
	POL+	27.8545		35.8456	27.9604	28.3110	36.0317

Table 2: Static First Hyperpolarizabilities (geometry/method)

Molecule	Basis	Gas Geometry			SCRF Geometry		
		gas	zern	scrf	gas	zern	scrf
HF	6-31G**	-8.229	-7.734	-8.649	-8.304	-7.804	-8.733
	pVDZ	-9.218	-8.772	-9.688	-9.307	-8.856	-9.786
	Sadlej	-4.106	-2.488	-2.940	-4.172	-2.538	-3.001
	POL+	-4.401	-2.540	-3.001	-4.468	-2.589	-3.061
H_2O	6-31G**	-17.031	-14.908	-21.255	-17.668	-15.410	-22.056
	pVDZ	-17.395	-15.324	-21.688	-17.846	-15.693	-22.30
	Sadlej	-7.533	7.856	13.500	-7.733	7.810	13.466
	POL+	-9.522	7.260	12.513	-9.674	7.237	12.516
HCN	6-31G**	-19.123	-18.605	-31.588	-19.296	-18.753	-31.955
	pVDZ	-25.331	-24.102	-40.543	-25.526	-24.261	-40.952
	Sadlej	0.095	27.010	50.272	-0.106	27.120	50.638
	POL+	-2.065	25.109	46.735	-2.260	25.222	47.093
CH_3CN	6-31G**	-21.429	-13.126	-16.417	-21.825	-13.444	-16.997
	pVDZ	-32.259	-22.127	-35.601	-32.554	-22.349	-36.064
	Sadlej	10.031	71.825	169.836	10.028	72.403	172.031
	POL+	9.687		169.966	9.679	71.611	170.682

Table 3: Static Second Hyperpolarizabilities

Molecule	Basis	Gas Geometry			SCRF Geometry		
		gas	zern	scrf	gas	zern	scrf
HF	6-31G**	24.4969	22.8757	27.5571	24.6650	23.0355	27.7847
	pVDZ	25.1817	23.6617	28.0813	25.3984	23.8653	28.3581
	Sadlej	235.9687	232.7408	279.4043	236.8560	233.5658	280.5249
	POL+	269.2070	263.5369	316.6789	270.2094	264.4685	317.9454
H_2O	6-31G**	109.3723	94.3637	172.9602	110.0734	94.6951	174.7522
	pVDZ	118.6161	101.5090	181.7827	119.4831	102.0332	183.8751
	Sadlej	837.9313	858.3272	1799.8793	833.8976	855.0305	1796.8119
	POL+	936.8293	944.3039	1983.3998	930.7612	939.5260	1977.5857
HCN	6-31G**	33.4662	26.9118	52.8463	34.1105	27.3383	54.1165
	pVDZ	70.0412	59.2491	117.3726	70.5800	59.5340	118.8143
	Sadlej	1909.0660	1984.4866	3944.1443	1919.2854	1996.2000	3981.3622
	POL+	1867.4501	1965.2312	3914.2968	1878.1392	1977.4493	3942.4103
CH_3CN	6-31G**	315.5950	309.2366	750.3814	316.7645	310.6964	757.0030
	pVDZ	502.3181	463.6660	1065.1033	503.2560	464.7043	1071.3015
	Sadlej	2993.3864	3403.6288	9124.6892	3011.3751	3430.5305	9241.1446
	POL+	2945.6121		9083.8205	2963.1648	3407.3024	9197.2817